Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

for the manuscript

"Desorption of hydrogen from light metal hydrides: concerted electronic rearrangement and role of H···H interactions"

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Computational Details. The geometry optimisations of the benchmark metal hydrides were each performed at the CCSD/6-311++G(d,p) level of approximation using the Gaussian09 software suite [1]. These calculations entailed constraining the H···H distances for both conformations, while the head-to-tail dimers that exhibited complete M-H bond cleavage required an addition M-H···H-M dihedral angle constraint to maintain a linear configuration. The subsequent topological analyses of the electron distributions and atomic properties were then carried out using the AIMALL software package [2].

[1] M.J. Frisch et al. Gaussian09, Revision A.02, Gaussian Inc., Wallingford, CT (USA), 2009

[2] T.A. Keith, *AIMALL*, version 13.05.06, TK Gristmill Software, 2013

Table S1. Decomposition temperature (T_{des}), Pauling electronegativity (χ), and standard redox potential ($E°$) values for selected metal hydrides.

Compound	T_{des} (°C)	χ (M)	$E°$ (V)
LiH	720	0.98	-3.04
NaH	425	0.93	-2.713
KH	417	0.82	-2.925
RbH	170	0.82	-2.924
CsH	170	0.79	-2.923
BeH_2	250	1.57	-1.97
MgH_2	327	1.31	-2.356
CaH_2	600	1.00	-2.84
SrH_2	675	0.95	-2.89
BaH_2	675	0.89	-2.92

[1] W. Grochala, P.P. Edwards, *Chem. Rev.*, 2004, **104**, 1283

[2] L. Pauling, "*The Nature of the Chemical Bond*"; 3rd, Cornell University Press: Ithaca, New York, 1960

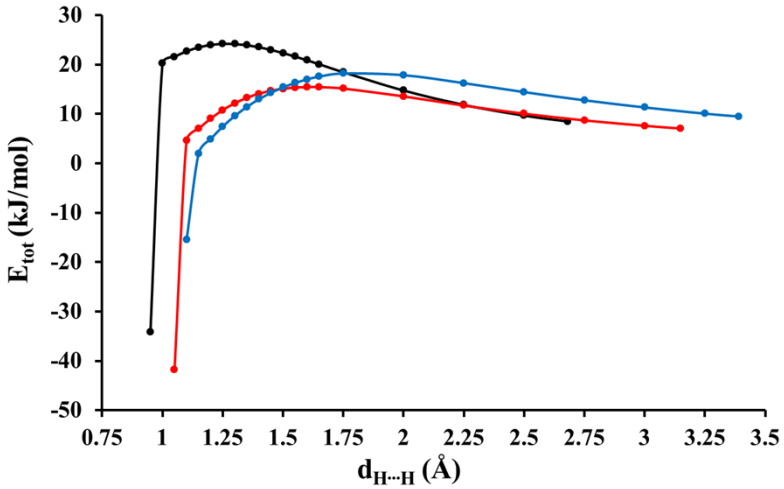

Figure S1. Internal energy profiles for the head-to-tail dimers of LiH (black), NaH (red), and KH (blue) *vs.* H···H distance.

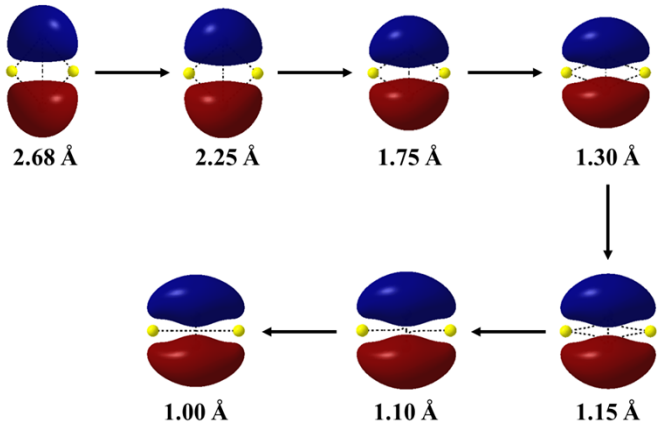

Figure S2. Plot of the highest occupied molecular orbital (HOMO) for **1** at a range of H···H separations. Isoelectronic density levels are 0.337 eÅ^{-3}.

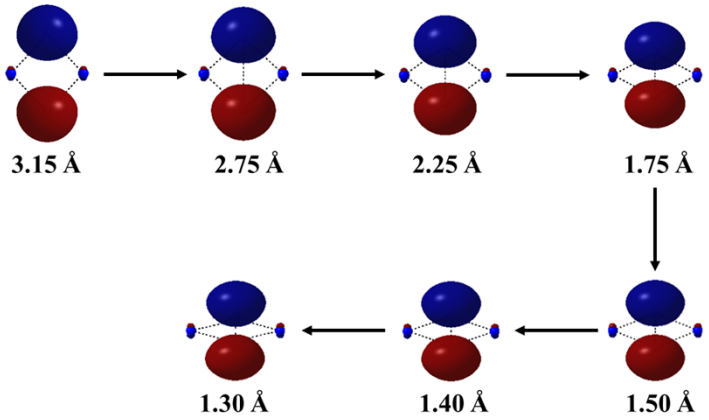

Figure S3. Plot of the highest occupied molecular orbital (HOMO) for **2** at a range of H···H separations. Isoelectronic density levels are 0.337 eÅ^{-3}.

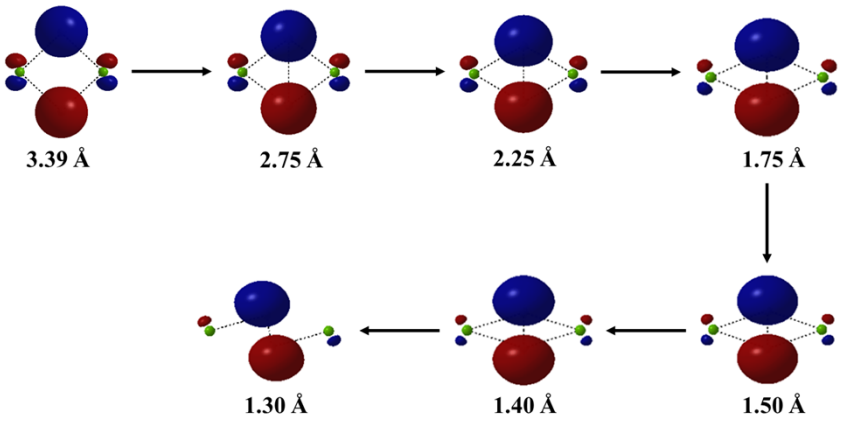

Figure S4. Plot of highest occupied molecular orbital (HOMO) for **3** at a range of H···H separations. Isoelectronic density levels are 0.337 eÅ^{-3}.

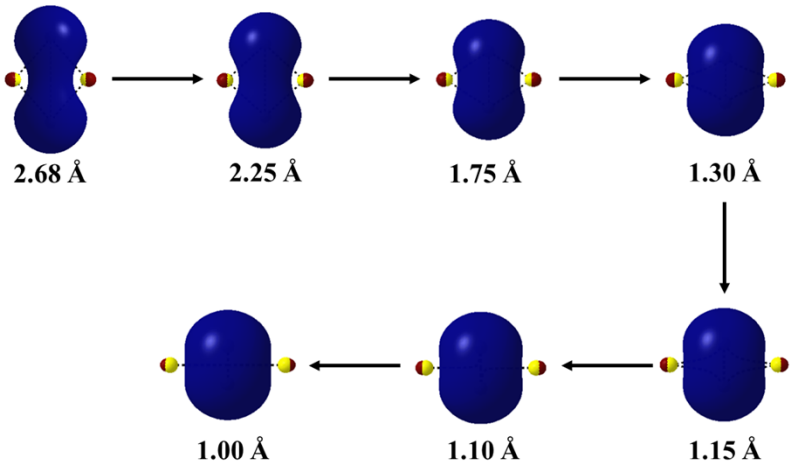

Figure S5. Plot of HOMO-1 for **1** at a range of H···H separations. Isoelectronic density levels are 0.337 eÅ^{-3}.

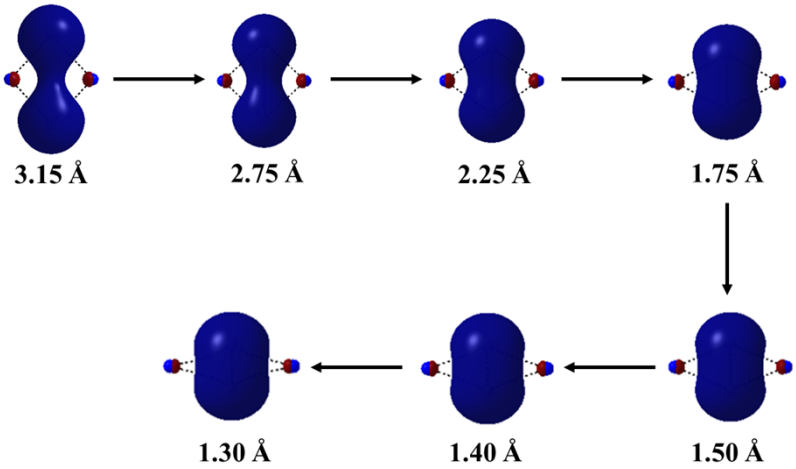

Figure S6. Plot of HOMO-1 for **2** at a range of H···H separations. Isoelectronic density levels are 0.337 eÅ^{-3}.

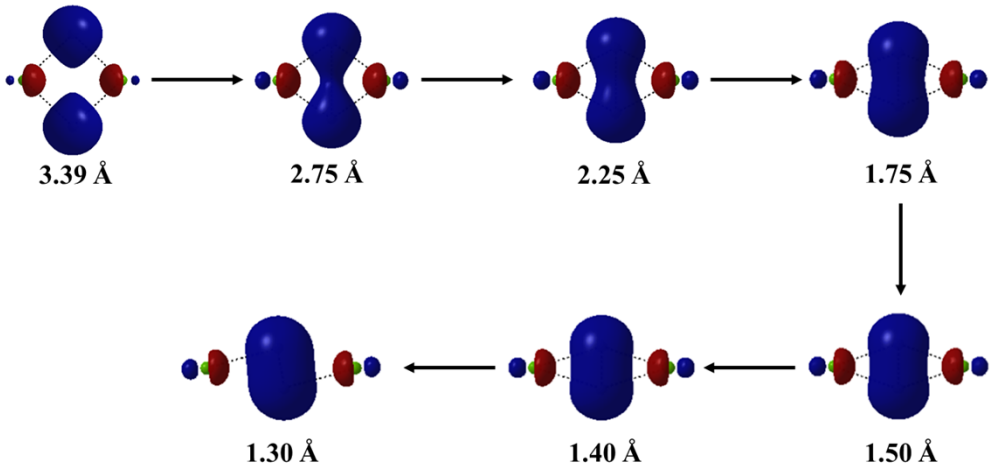

Figure S7. Plot of HOMO-1 for **3** at a range of H···H separations. Isoelectronic density levels are 0.337 eÅ^{-3}.

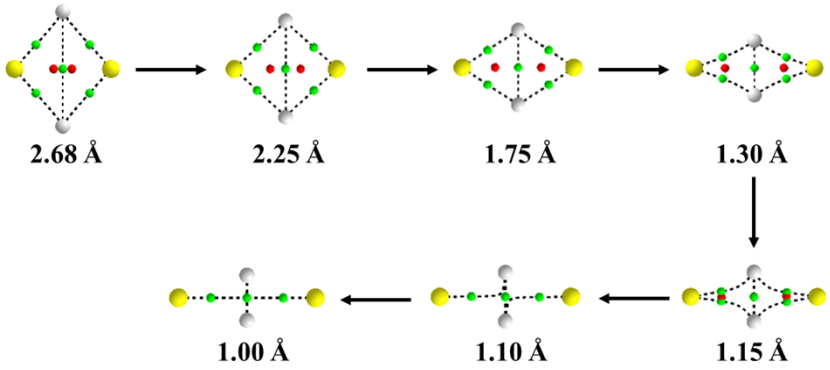

Figure S8. Molecular graphs for **1** at a range of H···H separations, with bond (BCP) and ring (RCP) critical points denoted as green and red spheres, respectively.

Table S2. Salient topological and atomic properties of the electron density for the M-H and H···H bonds in the rhombic and head-to-tail dimers of **1** at the CCSD/6-311++G(d,p) level of approximation.

	H···H			M-H					
d Å	$\rho_b(r)$ eÅ^{-3}	$\nabla^2\rho_b(r)$ eÅ^{-5}	d Å	$\rho_b(r)$ eÅ^{-3}	$\nabla^2\rho_b(r)$ eÅ^{-5}	q(M) au	q(H) au	V(M) au	V(H) au
				1					
3.50	0.072	0.205	2.08	0.121	1.269	0.90	-0.90	27	134
3.25	0.081	0.262	1.97	0.140	1.647	0.90	-0.90	26	128
3.00	0.093	0.319	1.87	0.161	2.115	0.90	-0.90	26	123
2.75	0.110	0.381	1.78	0.182	2.665	0.90	-0.90	25	119
2.68	*0.115*	*0.401*	*1.76*	*0.188*	*2.822*	*0.90*	*-0.90*	*25*	*118*
2.50	0.133	0.471	1.70	0.204	3.252	0.90	-0.90	24	115
2.25	0.165	0.637	1.64	0.222	3.800	0.90	-0.90	24	112
2.00	0.210	0.938	1.60	0.234	4.222	0.90	-0.90	24	110
1.75	0.279	1.357	1.58	0.240	4.511	0.89	-0.89	25	109
1.65	0.318	1.488	1.57	0.241	4.592	0.89	-0.89	25	109
1.60	0.341	1.518	1.57	0.241	4.619	0.89	-0.89	25	109
1.55	0.366	1.508	1.57	0.240	4.644	0.89	-0.89	25	110
1.50	0.395	1.444	1.57	0.240	4.689	0.89	-0.89	25	110
1.45	0.428	1.310	1.57	0.240	4.743	0.89	-0.89	26	110
1.40	0.465	1.085	1.57	0.238	4.772	0.88	-0.88	26	110
1.35	0.507	0.747	1.57	0.236	4.811	0.88	-0.88	26	111
1.30	0.553	0.276	1.58	0.235	4.857	0.88	-0.88	27	111
1.25	0.606	-0.349	1.58	0.233	4.933	0.88	-0.88	27	112
1.20	0.666	-1.150	1.58	0.232	5.021	0.87	-0.87	28	113
1.15	0.733	-2.145	1.59	0.230	5.127	0.87	-0.87	29	114
1.10	0.808	-3.343	1.59	0.229	5.236	0.86	-0.86	29	115
1.05	0.893	-4.761	1.60	0.227	5.282	0.86	-0.86	30	115
1.00	0.989	-6.414	1.61	0.223	5.297	0.85	-0.85	31	116
				Li-H···H-Li					
3.50	0.010	0.078	1.60	0.260	3.990	0.89	-0.89	26	130
3.25	0.015	0.116	1.60	0.260	3.975	0.89	-0.89	26	131
3.00	0.021	0.171	1.60	0.259	3.961	0.89	-0.89	26	132

2.75	0.031	0.244	1.61	0.258	3.941	0.89	-0.89	26	133
2.68	0.035	0.269	1.61	0.258	3.933	0.89	-0.89	26	133
2.50	0.046	0.343	1.61	0.256	3.908	0.88	-0.88	27	133
2.25	0.069	0.488	1.62	0.253	3.850	0.87	-0.87	27	131
2.00	0.104	0.720	1.63	0.247	3.743	0.86	-0.86	28	129
1.75	0.164	1.047	1.65	0.235	3.532	0.83	-0.83	30	126
1.65	0.200	1.149	1.66	0.228	3.400	0.82	-0.82	31	125
1.60	0.221	1.169	1.67	0.224	3.320	0.81	-0.81	32	124
1.55	0.246	1.155	1.68	0.219	3.228	0.79	-0.79	32	123
1.50	0.275	1.090	1.69	0.213	3.125	0.78	-0.78	32	122
1.45	0.307	0.957	1.70	0.207	3.007	0.76	-0.76	35	120
1.40	0.345	0.734	1.72	0.200	2.874	0.74	-0.74	36	119
1.35	0.388	0.397	1.73	0.192	2.723	0.71	-0.71	37	117
1.30	0.437	-0.082	1.75	0.183	2.553	0.68	-0.68	40	115
1.25	0.493	-0.731	1.78	0.173	2.362	0.65	-0.65	44	113
1.20	0.557	-1.582	1.80	0.161	2.147	0.62	-0.62	48	110
1.15	0.630	-2.668	1.84	0.148	1.903	0.57	-0.57	53	108
1.10	0.715	-4.029	1.89	0.133	1.625	0.52	-0.52	62	104
1.05	0.813	-5.720	1.95	0.113	1.301	0.46	-0.46	76	101
1.00	0.931	-7.866	2.06	0.088	0.894	0.36	-0.36	94	93
0.95	1.120	-11.874	6.35	0.000	0.000	0.00	0.00	143	49

The optimised structures of the rhombic dimers **1** are presented in *italics*. The topological values of the electron density for RCPs are presented in red.

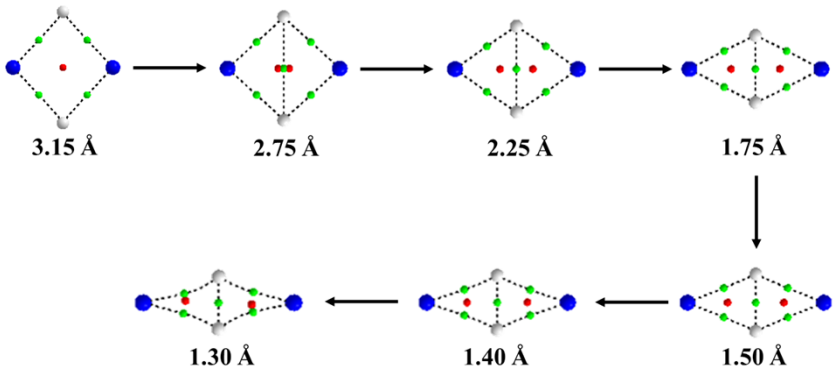

Figure S9. Plot of molecular graphs for **2** at a range of H···H separations, with bond (BCP) and ring (RCP) critical points denoted as green and red spheres, respectively.

Table S3. Salient topological and atomic properties of the electron density for the M-H and H···H bonds in the rhombic and head-to-tail dimers of **2** at the CCSD/6-311++G(d,p) level of approximation.

	H···H			M-H					
d Å	**ρ_b(r) eÅ^{-3}**	**$\nabla^2\rho_b$(r) eÅ^{-5}**	**D Å**	**ρ_b(r) eÅ^{-3}**	**$\nabla^2\rho_b$(r) eÅ^{-5}**	**q(M) au**	**q(H) au**	**V(M) au**	**V(H) au**
				2					
3.50	0.050	0.414	2.23	0.120	1.543	0.85	-0.85	63	128
3.25	0.056	0.400	2.15	0.135	1.876	0.85	-0.85	62	125
3.15	*0.059*	*0.397*	*2.12*	*0.140*	*2.009*	*0.85*	*-0.85*	*61*	*124*

3.00	0.063	0.398	2.08	0.148	2.210	0.85	-0.85	61	122
2.75	0.076	0.430	2.03	0.159	2.515	0.85	-0.85	60	121
2.50	0.095	0.520	1.99	0.168	2.763	0.86	-0.86	59	119
2.25	0.121	0.693	1.96	0.173	2.948	0.86	-0.86	58	118
2.00	0.162	0.979	1.94	0.175	3.052	0.86	-0.86	58	118
1.75	0.228	1.335	1.94	0.173	3.086	0.87	-0.87	58	118
1.65	0.267	1.421	1.94	0.171	3.087	0.87	-0.87	58	118
1.60	0.290	1.422	1.94	0.170	3.082	0.87	-0.87	59	118
1.55	0.317	1.379	1.95	0.169	3.081	0.87	-0.87	59	118
1.50	0.347	1.278	1.95	0.167	3.075	0.87	-0.87	59	118
1.45	0.381	1.099	1.95	0.166	3.075	0.87	-0.87	59	118
1.40	0.420	0.822	1.96	0.164	3.072	0.87	-0.87	59	118
1.35	0.463	0.423	1.96	0.163	3.074	0.87	-0.87	59	118
1.30	0.513	-0.124	1.96	0.159	3.051	0.87	-0.87	59	118
				Na-H···H-Na					
3.50	0.011	0.077	1.91	0.207	3.075	0.71	-0.71	71	121
3.25	0.016	0.115	1.91	0.206	3.062	0.70	-0.70	72	122
3.15	0.018	0.134	1.92	0.206	3.055	0.70	-0.70	72	122
3.00	0.022	0.168	1.92	0.206	3.043	0.69	-0.69	73	123
2.75	0.033	0.239	1.92	0.204	3.016	0.68	-0.68	74	122
2.50	0.048	0.331	1.92	0.203	2.975	0.67	-0.67	75	121
2.25	0.072	0.459	1.93	0.199	2.910	0.65	-0.65	76	119
2.00	0.109	0.654	1.94	0.194	2.799	0.62	-0.62	78	115
1.75	0.174	0.889	1.97	0.184	2.596	0.57	-0.57	82	110
1.65	0.213	0.924	1.98	0.178	2.471	0.55	-0.55	83	106
1.60	0.237	0.899	1.99	0.175	2.395	0.54	-0.54	84	105
1.55	0.264	0.831	2.00	0.170	2.309	0.52	-0.52	85	103
1.50	0.295	0.702	2.02	0.165	2.209	0.50	-0.50	87	102
1.45	0.331	0.493	2.03	0.160	2.097	0.48	-0.48	89	100
1.40	0.372	0.180	2.05	0.153	1.967	0.46	-0.46	90	97
1.35	0.418	-0.264	2.07	0.146	1.820	0.43	-0.43	92	96
1.30	0.471	-0.870	2.10	0.137	1.651	0.41	-0.41	96	93
1.25	0.532	-1.672	2.13	0.126	1.458	0.37	-0.37	99	90
1.20	0.601	-2.706	2.18	0.112	1.236	0.33	-0.33	105	87
1.15	0.682	-4.017	2.25	0.096	0.979	0.29	-0.29	112	84
1.10	0.776	-5.677	2.37	0.074	0.664	0.22	-0.22	122	79
1.05	0.914	-5.706	6.54	0.000	0.000	0.00	0.00	147	52

The optimised structures of the rhombic dimers **2** are presented in *italics*. The topological values of the electron density for RCPs are presented in red.

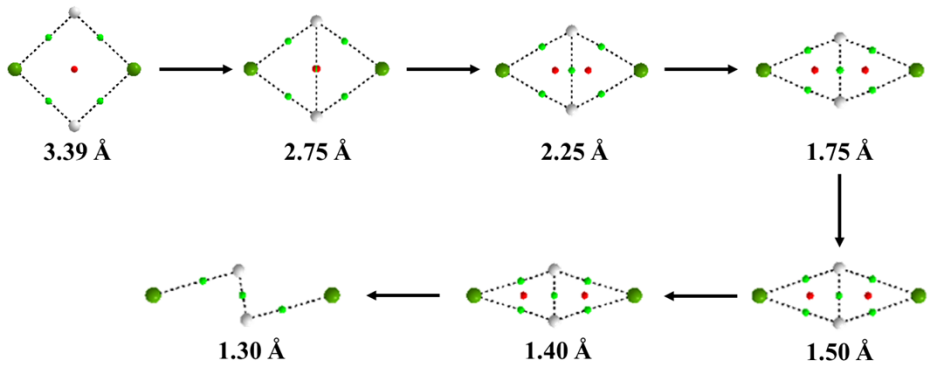

Figure S10. Plot of molecular graphs for **3** at a range of H···H separations, with bond (BCP) and ring (RCP) critical points denoted as green and red spheres, respectively.

Table S4. Salient topological and atomic properties of the electron density for the M-H and H···H bonds in the rhombic and head-to-tail dimers of **3** at the CCSD/6-311++G(d,p) level of approximation.

H···H			M-H						
d Å	$\rho_b(r)$ eÅ^{-3}	$\nabla^2\rho_b(r)$ eÅ^{-5}	d Å	$\rho_b(r)$ eÅ^{-3}	$\nabla^2\rho_b(r)$ eÅ^{-5}	q(M) au	q(H) au	V(M) au	V(H) au
				3					
3.50	0.039	0.359	2.49	0.127	1.232	0.82	-0.82	135	123
3.39	*0.041*	*0.355*	*2.46*	*0.132*	*1.306*	*0.82*	*-0.82*	*134*	*123*
3.25	0.044	0.353	2.43	0.137	1.390	0.82	-0.82	134	122
3.00	0.051	0.380	2.38	0.147	1.541	0.83	-0.83	133	119
2.75	0.063	0.443	2.34	0.156	1.676	0.83	-0.83	132	118
2.50	0.083	0.554	2.31	0.163	1.788	0.83	-0.83	132	117
2.25	0.110	0.730	2.29	0.168	1.875	0.83	-0.83	131	116
2.00	0.151	1.002	2.27	0.170	1.937	0.83	-0.83	131	115
1.75	0.219	1.315	2.27	0.169	1.978	0.83	-0.83	131	115
1.65	0.260	1.364	2.27	0.168	1.990	0.84	-0.84	131	115
1.60	0.284	1.341	2.27	0.166	1.994	0.84	-0.84	131	114
1.55	0.311	1.268	2.28	0.164	1.995	0.84	-0.84	132	114
1.50	0.343	1.133	2.28	0.163	2.007	0.84	-0.84	132	114
1.45	0.378	0.911	2.29	0.160	2.010	0.84	-0.84	132	114
1.40	0.418	0.581	2.29	0.158	2.013	0.83	-0.83	132	113
1.35	0.464	0.115	2.29	0.151	2.002	0.83	-0.83	132	113
1.30	0.520	-0.93	2.33	0.146	1.738	0.59	-0.59	141	97
				K-H···H-K					
3.50	0.013	0.085	2.26	0.192	1.857	0.69	-0.69	143	118
3.39	0.015	0.102	2.26	0.191	1.851	0.68	-0.68	143	119
3.25	0.018	0.124	2.26	0.191	1.843	0.68	-0.68	143	119
3.00	0.026	0.177	2.27	0.189	1.825	0.67	-0.67	144	119
2.75	0.037	0.245	2.27	0.187	1.799	0.65	-0.65	145	119
2.50	0.053	0.328	2.28	0.184	1.764	0.63	-0.63	148	117
2.25	0.078	0.441	2.29	0.179	1.710	0.60	-0.60	149	114
2.00	0.118	0.611	2.31	0.172	1.628	0.57	-0.57	150	110

1.75	0.185	0.802	2.35	0.160	1.490	0.51	-0.51	152	103
1.65	0.226	0.804	2.37	0.153	1.409	0.48	-0.48	153	100
1.60	0.251	0.758	2.38	0.149	1.360	0.47	-0.47	154	98
1.55	0.279	0.665	2.39	0.145	1.305	0.45	-0.45	154	97
1.50	0.311	0.505	2.41	0.139	1.241	0.43	-0.43	155	95
1.45	0.348	0.258	2.43	0.133	1.168	0.41	-0.41	157	93
1.40	0.389	-0.101	2.46	0.126	1.083	0.39	-0.39	160	91
1.35	0.437	-0.604	2.49	0.117	0.986	0.36	-0.36	162	89
1.30	0.492	-1.285	2.53	0.106	0.873	0.33	-0.33	163	87
1.25	0.555	-2.180	2.59	0.093	0.743	0.29	-0.29	166	83
1.20	0.627	-3.328	2,68	0.077	0.592	0.24	-0.24	171	80
1.15	0.711	-4.762	2.81	0.057	0.417	0.19	-0.19	175	76
1.10	0.826	-6.997	6.00	0.001	0.005	0.01	-0.01	180	54

The optimised structures of the rhombic dimers **3** are presented in *italics*. The topological values of the electron density for RCPs are present in red.

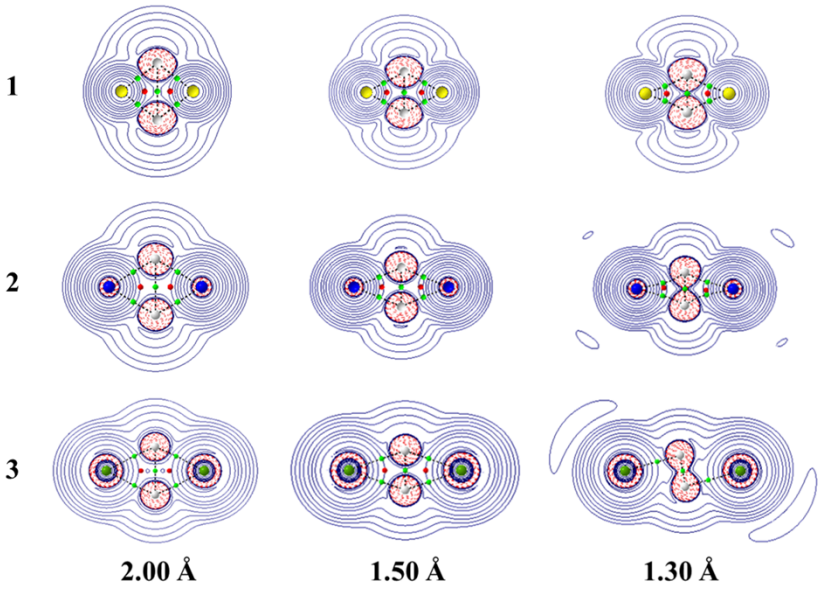

Figure S11. $\nabla^2\rho_b(\mathbf{r})$ plots of the rhombic dimers of **1-3** at a range of H···H separations. The positive (solid blue) and negative (dashed red) contours are plotted in increments of 2.4 x 10^{-2}, 4.8 x 10^{n}, 9.6 x 10^{n}, and 1.9 x 10^{n+1} (n = -2, -1, 0, 1, 2, and 3).

Table S5. Salient angles for the rhombic dimers of **1-3** at the CCSD/6-311++G(d,p) level of approximation.

	1		**2**		**3**	
d **Å**	**H-M-H** °	**M-H-M** °	**H-M-H** °	**M-H-M** °	**H-M-H** °	**M-H-M** °
3.50	115	65	104	76	90	91
3.39	-	-	-	-	*87*	*93*
3.25	111	56	98	82	84	96
3.15	-	-	*96*	*84*	-	-
3.00	107	53	92	88	78	102

2.75	101	51	85	95	72	108
2.68	*100*	*81*	-	-	-	-
2.50	94	86	78	102	66	115
2.25	86	94	70	110	59	121
2.00	77	103	62	118	52	128
1.75	67	113	54	126	45	135
1.65	63	117	50	130	43	137
1.60	61	119	49	131	41	139
1.55	59	121	47	133	40	140
1.50	57	123	45	135	38	142
1.45	55	125	44	136	37	143
1.40	53	127	42	138	36	145
1.35	51	129	40	140	33	147
1.30	49	131	39	142	31	149
1.25	47	133	-	-	-	-
1.20	45	135	-	-	-	-
1.15	42	138	-	-	-	-
1.10	40	140	-	-	-	-
1.05	38	142	-	-	-	-
1.00	36	144	-	-	-	-